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PERMEABLES.DWPI,EPAB,JPAB,USPT.	10
(3 AND (WATER ADJ PERMEABLE)).USPT,JPAB,EPAB,DWPI.	2
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<u>L4</u>	L3 AND (water ADJ permeable)	2	<u>L4</u>
<u>L3</u>	L2 AND acid	175	<u>L3</u>
<u>L2</u>	L1 AND chlorite	195	<u>L2</u>
<u>L1</u>	(chlorine ADJ dioxide) SAME (bag OR container OR device)	457	<u>L1</u>

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L4: Entry 1 of 2

File: USPT

May 29, 2001

US-PAT-NO: 6238643

DOCUMENT-IDENTIFIER: US 6238643 B1

TITLE: Method and device for the production of an aqueous solution containing chlorine dioxide

DATE-ISSUED: May 29, 2001

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Thangaraj; Appadurai	Colonia	NJ		
Speronello; Barry K.	Montgomery Township	NJ		
Wildman; Timothy D.	Monmouth Junction	NJ		

US-CL-CURRENT: 423/477; 252/187.21, 252/187.23

## ABSTRACT:

The present invention is generally directed to a method of producing an aqueous solution of chlorine dioxide from the reaction of a metal chlorite and an acid forming component which do not react to produce chlorine dioxide in the substantial absence of water. The reactants are separated from liquid water by a membrane which allows the controlled passage of liquid water and/or water vapor into contact with the reactants. The chlorine dioxide thus generated passes out through the membrane into the liquid water to produce the desired aqueous solution. Aqueous solutions containing chlorine dioxide produced in this manner can be conveniently used for commercial and domestic cleaning operations such as in the food industry.

33 Claims, 4 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 1

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	RWC	Draw Desc	Image
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☐ 2. Document ID: US 5922776 A

L4: Entry 2 of 2

File: USPT

Jul 13, 1999

US-PAT-NO: 5922776

DOCUMENT-IDENTIFIER: US 5922776 A

TITLE: Sustained release, transparent biocidal compositions

DATE-ISSUED: July 13, 1999

## INVENTOR-INFORMATION:

NAME	CITY	STATE	ZIP CODE	COUNTRY
Wellenghoff; Stephen T.	San Antonio	TX		
Kampa; Joel J.	San Antonio	TX		
Barenberg; Sumner A.	Chicago	IL		
Gray; Peter N.	Chicago	IL		

US-CL-CURRENT: 514/772.3; 106/15.05, 252/187.23, 424/405, 424/408, 424/409, 424/410, 424/412

**ABSTRACT:**

A composition for retarding bacterial, fungal and viral contamination and mold growth containing an acid releasing polymer, a hydrophilic material, and chlorite anions. Each component of the composition has a particle size of not more than about 1,000 angstroms. The composition is substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

59 Claims, 1 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 1

Full	Title	Citation	Front	Review	Classification	Date	Reference	Sequences	Attachments	Claims	KWIC	Draw Desc	Image
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L4: Entry 2 of 2

File: USPT

Jul 13, 1999

DOCUMENT-IDENTIFIER: US 5922776 A

TITLE: Sustained release, transparent biocidal compositions

Abstract Text (1):

A composition for retarding bacterial, fungal and viral contamination and mold growth containing an acid releasing polymer, a hydrophilic material, and chlorite anions. Each component of the composition has a particle size of not more than about 1,000 angstroms. The composition is substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

Brief Summary Text (4):

Chlorine dioxide or sodium chlorite have also been incorporated in food packaging. Studies have shown that residual levels of such preservatives do not result in a significant genetic or carcinogenic hazard to humans. Meier et al. studied the effect of subchronic and acute oral administration of chlorine, chlorine dioxide, sodium chlorite and sodium chlorate on the induction of chromosomal aberrations and spermhead abnormalities in mice [Environ. Mutagenesis, 7, 201 (1985)]. Only the highly reactive hypochlorite resulted in a weak positive effect for mutagenic potential. The other compounds, including chlorine dioxide and sodium chlorite, failed to induce any chromosomal aberrations or increased numbers of micronuclei in the bone marrow of mice. Vilagines et al. attribute the relatively innocuous effect of chlorine dioxide to its inability to produce halomethanes, unlike hypochlorite and chlorine [Proc. AWWA Disinfect. Semin., 24 pp. (1977); Chem. Abs. 93, 173513f]. Recently, Richardson et al. reported that an EPA study of the reaction of chlorine dioxide with water borne organics confirmed this observation [Environ. Sci. Technol., 28, 592 (1994)].

Brief Summary Text (5):

Japanese Kokai Nos. 63/296,758, 63/274,434, and 57/168,977 describe deodorants containing chlorine dioxide incorporated in a polymer, ceramic beads, or calcium silicate wrapped in nonwoven cloth, respectively. Gels that generate chlorine dioxide for use as topical applications for disinfection are disclosed by Kenyon et al., Am. J. Vet. Res., 45(5), 1101 (1986). Chlorine dioxide generating gels are generally formed by mixing a gel containing suspended sodium chlorite with a gel containing lactic acid immediately prior to use to avoid premature chlorine dioxide release. Chlorine dioxide releasing gels have also been used in food preservation.

Brief Summary Text (6):

Encapsulation processes have also been used in preparing sources of chlorine dioxide. Canadian Patent No. 959,238 describes generation of chlorine dioxide by separately encapsulating sodium chlorite and lactic acid in polyvinyl alcohol and mixing the capsules with water to produce chlorine dioxide.

Brief Summary Text (7):

Tice et al. U.S. Pat. No. 4,585,482 describes gradual hydrolysis of alternating poly(vinyl methyl ether-maleic anhydride) or poly(lactic-glycolic acid) to generate acid that can release chlorine dioxide from sodium chlorite. A polyalcohol humectant and water are encapsulated with the polyanhydride or polyacid in a nylon coating. After sodium chlorite is diffused into the capsule through the nylon wall, an impermeable polystyrene layer is coacervated around the nylon capsule to retain water within the capsule. The capsules can be coated onto surfaces to release chlorine dioxide. Although the capsules are said to provide biocidal action for several days to months, chlorine dioxide release begins immediately after the capsules are prepared. The batchwise process used to prepare the capsules also involves numerous chemical reactions and physical processes, some of which involve environmental disposal problems.

Brief Summary Text (8):

Wellinghoff et al. have formulated composites that include a hydrophobic phase containing an acid releasing agent and a hydrophilic phase containing chlorite anions. The composite is substantially free of water until it is exposed to moisture. Once exposed to moisture, acid and hydronium ions are generated in the hydrophobic phase. The hydronium ions migrate to the hydrophilic phase and react with chlorite anions to release chlorine dioxide from the composite. These composites are composed of and generate only FDA approved substances or substances generally recognized as safe. The composites can be used for food packaging and other applications where the substances can be ingested by or in contact with humans. These composites are described in U.S. Pat. Nos. 5,360,609, 5,650,466, 5,707,739, 5,631,300, 5,668,185, and 5,705,902.

Brief Summary Text (9):

Wellinghoff et al. U.S. patent application Ser. No. 08/924,684 discloses a composite formulated for maximum chlorine dioxide release in which the hydrophilic material contains an .alpha.-amino ether and a chlorite salt formed by reaction of an iminium chlorite and a base. Iminium chlorite is unstable to nucleophilic attack by the chlorite anion. When the iminium chlorite is reacted with a base, however, the more stable .alpha.-amino ether and chlorite salt are formed.

Brief Summary Text (10):

Wellinghoff et al. U.S. Pat. No. 5,639,295 describes a method for maximizing chlorine dioxide release from an amine-containing composite by omitting the chlorite source until the composite is applied to a surface. After application, the composite is exposed to chlorine dioxide gas that either reacts with the amine to form iminium chlorite in situ or dissolves in the amine to provide chlorite anions. The composite is then activated in the presence of moisture to release chlorine dioxide. The composite can be exposed to elevated temperatures during processing, storage and application because the hydrophilic material does not contain iminium chlorite or any chlorite anions that could decompose at such temperatures. The method also precludes premature release of chlorine dioxide from the composite.

Brief Summary Text (12):

Although the Wellinghoff et al. composites are effective biocides, there is a need for biocidal compositions in which the acid releasing component and the chlorite containing component form an optically transparent or translucent, single-phase mixture.

Brief Summary Text (15):

The present invention is directed to a composition for retarding bacterial, fungal and viral contamination and mold growth containing an acid releasing polymer, a hydrophilic material and chlorite anions as components. Each component of the composition has a particle size of not more than about 1,000 angstroms, and is substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

Brief Summary Text (16):

Another embodiment of the present invention is directed to a composition for retarding bacterial, fungal and viral contamination and mold growth comprising an amide, chlorite anions, and an acid releasing terpolymer formed from polyvinylpyrrolidone, lactic acid and glycolic acid. Each component of the composition has a particle size of not more than about 1,000 angstroms, and is substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

Brief Summary Text (18):

Another embodiment of the invention is directed to a multilayered composite for providing sustained release of chlorine dioxide. The composite contains a water-soluble layer comprising an acid releasing polymer, a hydrophilic material and chlorite anions, an upper moisture regulating layer in contact with an upper surface of the water-soluble layer, and a lower moisture regulating layer in contact with a lower surface of the water-soluble layer. The water-soluble layer is substantially free of water and each component of the layer has a particle size of not more than about 1,000 angstroms. The moisture regulating layers are water insoluble, such that moisture permeating either of the moisture regulating layers hydrolyzes the acid releasing polymer to initiate release of chlorine dioxide from the multilayered composite.

Brief Summary Text (19):

Yet another embodiment of the invention is directed to a process for preparing a composition by mixing a hydrophilic material, a chlorite salt, an acid releasing

polymer and an organic solvent to form a mixture in which each component has a particle size of not more than about 1,000 angstroms, the mixture being substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

Brief Summary Text (20):

Another embodiment of the invention is directed to a process of preparing an acid releasing polymer by mixing a polyvinylpyrrolidone oligomer, lactic acid, glycolic acid and water, and heating the mixture in the presence of an esterification catalyst to form a polyvinylpyrrolidone-lactic acid-glycolic acid terpolymer having acid end groups. The terpolymer is dissolved in an organic solvent, and neutralized to esterify acid end groups of the terpolymer to form the acid releasing polymer.

Detailed Description Text (2):

In accordance with the present invention, it has been discovered that sustained release of chlorine dioxide can be generated from a solution containing chlorite anions when the solution is exposed to moisture. Although chlorine dioxide releasing compositions are known, this solution is unique because it is optically transparent or translucent and is essentially unnoticeable when applied to a substrate. When the solution has been applied to a substrate, the substrate can clearly be seen through the film formed on the substrate. If the solution, for example, is coated onto a containerboard box printed with graphics, the graphics remain clearly visible through the coating. Although the coating releases chlorine dioxide oxidant, the coating does not alter the graphics or effect the color of the graphics. The solution can also be coated on a surface of a transparent or translucent substrate to provide biocidal action while maintaining the "see-through" quality of the substrate. If the solution is coated onto a clear plastic food container, for example, a consumer can see the food within the container before purchasing the food. The biocidal solution protects the food from microbial contamination while allowing consumers to inspect the food without opening the container. The solution, therefore, allows visual inspection of a material while releasing chlorine dioxide to sterilize, deodorize, or protect the material from contamination or infestation.

Detailed Description Text (4):

Chlorine dioxide is released from the composition when an acid releasing polymer within the composition is hydrolyzed by adsorbed moisture, and releases acid and hydronium ions. The hydronium ions diffuse from the polymer to react with the chlorite anions in the composition to release chlorine dioxide gas. The chlorine dioxide gas diffuses out of the composition into the surrounding atmosphere for a period of up to about six months in order to prevent the growth of bacteria, molds, fungi and viruses on a material. The single-phase compositions provide more complete conversion to chlorine dioxide than is provided by two-phase compositions because the acid releasing polymer and chlorite anions are in a closer proximity to each other than in a two-phase composite. Compositions that release at least about 1.0.times.10.sup.-6 mole chlorine dioxide/cm.sup.2 for a period of at least one week, one month or six months can be formulated by the processes of the present invention for a variety of end uses.

Detailed Description Text (5):

Preferably, the composition comprises between about 0.1 wt. % and about 20 wt. % of chlorite anions and counterions, between about 10 wt. % and about 70 wt. % of a hydrophilic material, and between about 1.0 wt. % and about 50 wt. % acid releasing polymer, more preferably between about 10 wt. % and about 20 wt. % chlorite anions and counterions, between about 10 wt. % and about 50 wt. % hydrophilic material, and between about 10 wt. % and about 30 wt. % acid releasing polymer.

Detailed Description Text (6):

Any acid releasing polymer that forms a solution with the chlorite anions and counterions and the hydrophilic material and is capable of being hydrolyzed by ambient moisture is acceptable for purposes of the present invention. Preferably, the acid releasing polymer does not exude or extract into the environment. The acid releasing polymer preferably has a number average degree of polymerization of between about 10 and about 10,000, more preferably between about 50 and about 1000, and most preferably between about 100 and about 300.

Detailed Description Text (7):

The acid releasing polymer is preferably copolymerized with a hydrophilic oligomer to compatibilize the acid releasing polymer with the chlorite anions and the hydrophilic material. A preferred acid releasing polymer is a copolymer of a phase compatibilizing oligomer such as polyvinylpyrrolidone, polyvinyl alcohol, polyanhydride, or

polyacrylamide, and an acid such as lactic acid, glycolic acid, or other  $\alpha$ -hydroxy acids or mixtures of these acids. Preferred polyanhydrides have the formula: ##STR3## wherein R is: ##STR4## m is 1 or 2, n is an integer from 4 to 12, and X is O or N--CH.sub.3.

Detailed Description Text (8):

A particularly preferred acid releasing polymer is a terpolymer of polyvinylpyrrolidone, lactic acid and glycolic acid. Each of the lactic acid, glycolic acid and polyvinylpyrrolidone portions of the terpolymer preferably has a number average degree of polymerization of between about 1 and about 5,000, more preferably between about 5 and about 50 and, most preferably, between about 10 and about 30.

Detailed Description Text (9):

The most preferred acid releasing polymer has the formula: ##STR5## wherein PVNP has the formula: ##STR6## R is a lower alkyl group or a lower alkyl ester, n is from 5 to 500, x is from 1 to 5,000, y is from 0 to 5,000, and z is from 0 to 5,000, provided that either y or z must be at least one. R is preferably a methyl group, n is preferably 5 to 100, and x, y and z are preferably 1 to 1,000. The optimum proportions of lactic acid, glycolic acid and polyvinylpyrrolidone in the terpolymer are selected based upon the adhesiveness, stiffness, or other properties required for a desired application of the composition. One of ordinary skill in the polymer art would know how to optimize the proportions of lactic acid, glycolic acid and polyvinylpyrrolidone in the copolymer to obtain desired properties in the composition.

Detailed Description Text (10):

Any hydrophilic material that forms a solution with the chlorite anions and counterions and the hydrophobic material is acceptable for purposes of the present invention. The hydrophilic material is preferably an amide, an amine, or a polyhydric alcohol. When the chlorite source is a chlorite salt, the salt dissociates in the hydrophilic material to form chlorite anions and counterions. However if the hydrophilic material is an amine and the chlorite source is chlorine dioxide gas, the chlorine dioxide reacts with the amine to form iminium chlorite in situ, if the oxidation potential of the amine is sufficiently low for the amine to be oxidized.

Detailed Description Text (11):

The composition of the present invention preferably includes an amide as the hydrophilic material to provide adhesive properties to the composition. The amide is preferably selected from the group consisting of urea or oligomeric amides. Urea is most preferred because its high hydrogen bonding density improves the chlorine dioxide uptake and release efficiency of the composition, it dissolves in and plasticizes polyvinylpyrrolidone, it will not react with the acid releasing polymer, and it provides greater tackiness in the composition. The composition can include up to about 30 wt. % amide, preferably between about 5 and about 20 wt. % amide and, more preferably, between about 10 and about 15 wt. % amide.

Detailed Description Text (12):

The chlorite anions generally do not react with the hydrophilic material or the acid releasing polymer, but are surrounded by hydrogen bonds contributed by the nitrogen or hydroxide within the hydrophilic material or acid releasing polymer. Suitable chlorite sources that can be incorporated into the composition of the present invention include alkali metal chlorites such as sodium chlorite or potassium chlorite, alkaline-earth metal chlorites such as calcium chlorite, chlorite salts of a transition metal ion or a protonated primary, secondary, tertiary or quaternary amine or iminium chlorite salts. Many chlorite sources, such as sodium chlorite, are stable at processing temperatures in excess of about 100.degree. C., allowing for processing at relatively high temperatures.

Detailed Description Text (13):

The components of the composition are substantially free of water to avoid significant release of chlorine dioxide prior to use of the composition. For purposes of the present invention, the composition is substantially free of water if the amount of water in the composition does not provide a pathway for transmission of hydronium ions from the acid releasing polymer to the chlorite anions. Generally, the components of the composition can include up to a total of about 1.0 wt. % water without providing such a pathway for transmission of hydronium ions. Preferably, each component contains less than about 0.1 wt. % water, and, more preferably, between about 0.01 wt. % and about 0.1 wt. % water. Insubstantial amounts of water can hydrolyze a portion of the acid releasing polymer to produce acid and hydronium ions within the composition. The hydronium ions, however, do not diffuse to the chlorite anions until enough free water

is present for transport of hydronium ions.

Detailed Description Text (14):

A preferred composition of the present invention includes between about 10 wt. % and about 30 wt. % of a polyvinylpyrrolidone-lactic acid-glycolic acid terpolymer, between about 10 wt. % and about 30 wt. % urea, between about 10 wt. % and between about 20 wt. % chlorite anions, and between about 10 wt % and about 30 wt. % polyvinylpyrrolidone homopolymer.

Detailed Description Text (15):

The composition can also include a compatibilizer to compatibilize the acid releasing polymer with the hydrophilic material and chlorite anions within the composition. A compatibilizer is preferably added when the acid releasing polymer does not include a significant hydrophilic oligomer portion to compatibilize the polymer to the remainder of the composition. Preferred compatibilizers include polyvinylpyrrolidone homopolymer, or its copolymers with alkene oligomers. Polyvinylpyrrolidone is a preferred compatibilizer and also serves to increase the mechanical strength of the composition. The polyvinylpyrrolidone preferably has a number average degree of polymerization between about 1 and about 10,000, more preferably between about 100 and about 10,000 and, more preferably between about 300 and about 5,000.

Detailed Description Text (16):

A plasticizer can be added to the composition to soften the acid releasing polymer. The plasticizer is preferably any monomeric or oligomeric amide generally known in the polymer art as a plasticizer, such as succinamide, formamide, N-methyl formamide, and N-methylacetamide, and isopropylacrylamide-acrylamide. Formamide and N-methyl formamide are toxic and would not be preferred in applications involving human contact. If the polymer amine center is sufficiently mobile, the addition of a plasticizer is unnecessary. A glassy polymer can be softened to increase mobility by adding at least about 10 wt. %, preferably between about 10 and about 30 wt. % of a plasticizer to the polymer to lower glass transition temperature below the reaction temperature. Other amides that can be used as plasticizers for the acid releasing polymer of the invention include  $H_{sub.2}NC(O)(CH_{sub.2}CH_{sub.2}O)_{sub.n}CH_{sub.2}CH_{sub.2}C(O)NH_{sub.2}$  wherein n is 1 to 10,  $H_{sub.2}NC(O)(CH_{sub.2}CH_{sub.2}O)_{sub.n}CH((OCH_{sub.2}CH_{sub.2})_{sub.m}C(O)NH_{sub.2})_{sub.2}$  wherein n is 1 to 5 and m is 1 to 5, and  $N(CH_{sub.2}CH_{sub.2}O)_{sub.n}CH_{sub.2}CH_{sub.2}(O)NH_{sub.2})_{sub.3}$  wherein n is 1 to 10.

Detailed Description Text (17):

A moisture scavenger, such as sodium sulfate, calcium sulfate, silica gel, alumina, zeolites, and calcium chloride can be added to the composition to prevent premature hydrolysis of the acid releasing polymer. Humectants can be added to render the composition more hydrophilic and increase the rate of hydrolysis of the acid releasing polymer. Conventional film forming additives can also be added to the composition as needed. Such additives include crosslinking agents, flame retardants, emulsifiers and compatibilizers. These additives must be hydrophilic and soluble within the composition if the composition is to be optically transparent or translucent.

Detailed Description Text (19):

Suitable amines for use as the hydrophilic material include primary amines, secondary amines, and tertiary amines having pendant hydrogen bonding groups. An amine substituted with electron donating groups that donate electrons to convert chlorine dioxide to chlorite is preferred. Electron withdrawing groups concentrate electron density at such groups such that it is difficult for the chlorine dioxide to extract an electron from the amine. Tertiary amines having non-hydrogen bonding pendant groups that are dissolved in a hydrophilic solvent are also acceptable. Representative amines include: alkanolamines; copolymers of aminoalkanes and alkene bisacrylamides; alkylaminopyridine; alkene diamines; alkylamino cycloalkanes; alkylamino-carboxyamido alkanes dissolved in a diluent; amines having the formula  $R_{sub.3-x}NH_{sub.x}$ ;  $R_{sub.1}R_{sub.2}NCH_{sub.2}CH_{sub.2}C(O)NH_{sub.2}$ ; solubilized  $N(CH_2CH_{sub.2}OH)_{sub.3-x}$   $H_{sub.x}$ ,  $R_{sub.3}N(NCH_{sub.2}CH_{sub.2}C(O)NH_{sub.2})_{sub.2}$ ,  $(CH_{sub.3})_{sub.2}$ ,  $N(CH_{sub.2})_{sub.2}N(CH_{sub.3})_{sub.2}$ ,  $R_{sub.5}R_{sub.6}N(CH_{sub.2})_{sub.2}NHC(O)NH_{sub.2}$ ,  $N(CH_{sub.2}CH_{sub.2}NHC(O)NH_{sub.2})_{sub.3}$ , or ##STR7## wherein: R substituents are, independently,  $-(CH_{sub.2}CH_{sub.2}O)_{sub.y}H$ ,  $-C(CH_{sub.3})_{sub.2}(CH_{sub.2})_{sub.z}OH$ ,  $-(CH_{sub.2})_{sub.z}NH(CH_{sub.2}CH_{sub.2}O)_{sub.z}H$ ,  $-CH(CH_{sub.3})_{sub.2}$ , ##STR8## alkyl, cyvloalkyl, benzyl, acrylamide, or pyridyl;  $R_{sub.1}$ ,  $R_{sub.2}$ ,  $R_{sub.5}$ , and  $R_{sub.6}$  are alkyl;  $R_{sub.3}$  is methyl or ethyl; m is 1-100; n is 2 or 3; x is 0, 1 or 2; y is 1 or 2; and z is 1, 2 or 3. Generally, the above compounds can be solubilized in formamide, isopropylacrylamide-acrylamide or other conventional plasticizers.

Detailed Description Text (20):

Preferred amines include monoethanolamine, diethanolamine, triethanolamine, a copolymer of 1,3-diaminopropane or 1,2-diaminoethane and N,N-methylene bisacrylamide, 4-dimethylaminopyridine, tetramethylene ethylene diamine, N,N-dimethylamino cyclohexane, solubilized 1-(N-dipropylamino)-2-carboxyamido ethane or 1-(N-dimethylamino)-2-carboxyamido ethane, a primary amine having the formula R.sub.1 NH.sub.2, a secondary amine having the formula R.sub.2 R.sub.3 NH, N(CH.sub.2 CH.sub.2 OH).sub.3, ##STR9## solubilized NR.sub.5 R.sub.6 R.sub.7, (CH.sub.3).sub.2 NCH.sub.2 CH.sub.2 N(CH.sub.3).sub.2, R.sub.8 R.sub.9 NCH.sub.2 CH.sub.2 C(O)NH.sub.2, R.sub.11 R.sub.12 N(CH.sub.2).sub.3 NHC(O)NH.sub.2, N(CH.sub.2 CH.sub.2 NHC(O)NH.sub.2).sub.3, ##STR10## wherein: R.sub.1 is --CH.sub.2 CH.sub.2 OCH.sub.2 CH.sub.2 OH, --C(CH.sub.3).sub.2 CH.sub.2 OH, --CH.sub.2 CH.sub.2 NHCH.sub.2 CH.sub.2 OH, --CH(CH.sub.3).sub.2, --CH.sub.2 CH.sub.2 OH, ##STR11## or ##STR12## R.sub.2 and R.sub.3 are, independently, n-propyl, isopropyl, acrylamide, or --CH.sub.2 CH.sub.2 OH; R.sub.5 and R.sub.6 are methyl; R.sub.7 is 4-pyridyl; R.sub.8 and R.sub.9 are, independently, methyl, n-propyl or isopropyl; R.sub.11 and R.sub.12 are, independently, methyl, ethyl, n-propyl or isopropyl; m is an integer from 1 to 100; and n is 2 or 3. Suitable diluents include formamide or acrylamide-isopropyl acrylamide. Oligomeric or polymeric secondary amines converted to acrylamide substituted tertiary amines by Michael reaction with acrylamides are also suitable because the amide group does not react with the acid releasing agent.

Detailed Description Text (22):

The compositions of the present invention are prepared by mixing the hydrophilic material, a chlorite salt, the acid releasing polymer and an organic solvent to form a mixture having a particle size of not more than about 1,000 angstroms. The mixture is substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

Detailed Description Text (23):

The acid releasing polymer is prepared by mixing an oligomer, a carboxylic acid and water to form a mixture. The mixture is heated in the presence of an esterification catalyst to form a copolymer having acid end groups. The copolymer is dissolved in an organic solvent and neutralized to esterify the acid end groups to form the acid releasing polymer. A preferred acid releasing terpolymer is formed by mixing a polyvinylpyrrolidone oligomer, lactic acid, glycolic acid and water to form a mixture, heating the mixture in the presence of an esterification catalyst to form a polyvinylpyrrolidone-lactic acid-glycolic acid terpolymer having acid end groups, dissolving the terpolymer in an organic solvent, and neutralizing the terpolymer to esterify acid end groups of the terpolymer to form the acid releasing polymer. The preparation of this terpolymer is described in Example 2.

Detailed Description Text (24):

The esterification catalyst is preferably selected from the group consisting of p-toluene sulfonic acid, or other strong protic acids (i.e., acids that make an aqueous solution having a pH not greater than 1).

Detailed Description Text (25):

An organic solvent is suitable for preparing the compositions of the invention if the chlorite salt is substantially soluble in the organic solvent and the solvent is substantially free of water. The organic solvent is preferably methanol or ethanol, and is most preferably methanol.

Detailed Description Text (26):

A preferred solution includes between about 10 wt. % and about 30 wt. % of a polyvinylpyrrolidone-lactic acid-glycolic acid terpolymer, between about 10 wt. % and about 30 wt. % urea, between about 10 wt. % and between about 30 wt. % chlorite anions, between about 10 wt % and about 30 wt. % polyvinylpyrrolidone homopolymer, and between about 30 wt. % and about 60 wt. % methanol. The methanol in the solution evaporates when the solution is cast as a film or formed into some other end product.

Detailed Description Text (27):

Chlorine dioxide is released, for example, from this preferred composition by exposing the composition to moisture. The moisture hydrolyzes the acid releasing terpolymer, forming polyvinylpyrrolidone oligomer, lactic acid and glycolic acid within the composition. The lactic acid and glycolic acid react with water to form hydronium ions. The hydronium ions react with a chlorite salt to form chlorine dioxide and metal salts of lactic or glycolic acid. The hydrolysis is illustrated below: ##STR13##

Detailed Description Text (28):

The rate of chlorine dioxide release from a composition can be controlled when preparing the composition by changing the viscosity of the composition, changing the concentration of acid releasing polymer in the composition, changing the crystallinity of the components in the composition, and by adding a desiccant or humectant to the composition to control release of chlorine dioxide from the composition once it is exposed to moisture. The rate of chlorine dioxide release can be controlled during use by changing the temperature or moisture content of the composition.

Detailed Description Text (29):

The compositions of the present invention that contain an amine can form iminium chlorite rather than dissolved chlorite anions. Iminium chlorite is formed when the amine hydrophilic material is in contact with the hydrophobic acid releasing polymer. Chlorine dioxide (ClO.sub.2) is reduced by extracting an electron from the amine, forming an aminium radical cation and a chlorite counterion (ClO.sub.2.sup.-). The aminium cation quickly converts to an iminium cation by loss of a proton from an adjacent carbon atom and oxidation by another chlorine dioxide molecule. The mechanism for above reaction in an aqueous system is described by Rosenbatt et al., J. Org. Chem., 28, 2790 (1963); J. Amer. Chem. Soc. 89(5), 1158, 1163 (1967).

Detailed Description Text (30):

High chlorine dioxide to chlorite conversions are obtained if the chlorite anion and/or iminium cation that is generated by the initial electron transfer from the amine is rapidly complexed and stabilized by a hydrophilic molecule. In some formulations, uncomplexed chlorite anion may be depleted by subsequent reactions with the iminium counterion at temperatures above about 60.degree. C. Chlorites are also subject to disproportionation into chloride and chlorate. An amine with a high pK.sub.a is preferred because it reacts more rapidly with chlorine dioxide and acts as a more effective proton sink, maintaining the basic pH required for chlorite ion stability.

Detailed Description Text (31):

Chlorine dioxide is released from iminium chlorite when moisture contacts the composition. Hydrolysis of the acid releasing polymer provides hydronium cations (H.sub.3 O.sup.+) that react with iminium chlorite to release chlorine dioxide gas. The decomposition products of the reaction are aminium chloride salts and organic carboxylates. These products are retained within the composition.

Detailed Description Text (32):

It has been found that, in some instances, iminium chlorite may decompose if the composition is exposed to temperatures exceeding about 60.degree. C., reducing the available chlorite concentration for conversion to chlorine dioxide. In order to maximize chlorine dioxide release from the composite, it has been discovered that the chlorite source can be omitted from the composition until the composition is applied to a surface when the hydrophilic material in the composition is an amine. After application, the composition is exposed to chlorine dioxide gas that either reacts with the amine to form iminium chlorite in situ or dissolves in the amine to provide chlorite anions. The composition is then activated in the presence of moisture to release chlorine dioxide. The composite can be exposed to elevated temperatures during processing, storage and application because the hydrophilic material does not contain iminium chlorite or any chlorite anions that could decompose at such temperatures. The method also precludes premature release of chlorine dioxide from the composite. Chlorine dioxide can be provided on site by passing the composition through a chlorine dioxide generator.

Detailed Description Text (33):

In order for an amine to form iminium chlorite in neat form or in the presence of a plasticizer, the amine must be sufficiently electron rich and the amine nitrogen must be locally mobile. Electron withdrawing groups should be separated from the amine center by at least two methylene groups in order for the chlorine dioxide to extract an electron from the amine. Movement of the bonds about the nitrogen center of the amine is required for aminium formation. If the amine is frozen into a glassy matrix, the amine nitrogen will not be mobile and the amine will not convert to iminium chlorite. A glassy amine can be softened to increase mobility by adding at least about 10 wt. % of a plasticizer, such as a low molecular weight amide, to the amine to lower glass transition temperature below the reaction temperature. Other suitable plasticizers are well known in the polymer art.

Detailed Description Text (34):

Maximum chlorine dioxide release from a composition can be achieved by stabilizing the

chlorite anion. Iminium chlorite is unstable to nucleophilic attack by the chlorite anion. It has been discovered that the room temperature lifetime of chlorite anion is substantially extended when a strong base, such as a metal alkoxide, is present in the hydrophilic material containing the iminium chlorite. The mechanism of alkoxide stabilization of the chlorite counterion is shown below. ##STR14## wherein R'.sub.2 and R.sub.2 are groups that correspond to those of the selected amine and R" is an alkyl or hydrogen group. In the absence of water, the iminium ion is immediately decomposed into an .alpha.-amino ether and a more stable sodium chlorite salt. If water is present during the oxidation of the tertiary amine, an unstable .alpha.-amino alcohol is formed that can attack the chlorite anion unless the chlorite anion has been effectively complexed by the hydrophilic solvent. Addition of water after salvation of the chlorite ion is not as deleterious.

Detailed Description Text (35):

Acceptable strong bases for use in stabilizing the chlorite include metal alkoxides such as sodium, potassium or calcium methoxides, ethoxides, propoxides or butoxides, metal oxides such as aluminum oxide, or sodium oxide, metal ions such as Na.sup.+, trialkyl ammonium salts of alkoxides, ammonium salts of alkoxides, acetates such as sodium acetate, substituted acetates, or other materials that would generate a strong basic reaction to attack the nitrogen center of iminium chlorite.

Detailed Description Text (37):

The composition of the invention can be formulated as a powder. Although the powder is not optically transparent, it provides a slow rate of release of a low concentration of chlorine dioxide as compared to chlorite particles coated with a hydrophobic material. To prepare the powder, anhydrous particles are fed into a fluidized bed. A solution of the acid releasing polymer, the hydrophilic material and chlorite anions in an organic solvent as described above is aerosolized by passing the material through small diameter nozzles into the chamber of the fluidized bed where it can impinge upon the fluidized anhydrous particles. Upon contact with the fluidized particles, the chlorine dioxide releasing powder is formed as the solution solidifies to form an acid releasing core having a layer of anhydrous particles embedded in the outer surface thereof. Aggregation is minimized because the anhydrous particles are hard inorganic materials. The particles can then be packaged in a dry sealed container.

Detailed Description Text (40):

The compositions can also be used in forming a multilayered composite 10 including a water-soluble, optically transparent or translucent layer 12 comprising an acid releasing polymer, chlorite anions, and a hydrophilic material as shown in FIG. 1. The water-soluble layer 12 is cast onto a moisture regulating layer 14 on a substrate 16, and a moisture regulating layer 18 is then cast onto the water-soluble layer 12. The moisture regulating layers 14 and 18 are water-insoluble, water-permeable films, that prevent the water-soluble layer 12 from degrading in the presence of moisture. This arrangement enables a chlorine dioxide atmosphere to be provided over a period of days, weeks or months. The moisture regulating layers also control the rate of moisture ingress into the water-soluble layer to control chlorine dioxide release from the multilayered composite when activated by moisture. Suitable water-insoluble, water-permeable films can be composed of poly(ethylene-propylene) or poly(acrylic-ester acrylate) copolymers or ionomers thereof such as sulfonated salts of poly(ethylene-propylene). Hydroxyethylmethacrylate, methoxyethylmethacrylate, copolymers of at least one hydrophilic component and at least one hydrophobic component, and other water-insoluble, water-permeable films well known in the art are also suitable.

Detailed Description Text (41):

The layered composites of the present invention are intended to maintain a desired rate of chlorine dioxide release (moles/sec/cm.sup.2 of film) in the presence of atmospheric moisture at a surface for a length of time required for chlorine dioxide to absorb onto the surface and kill bacteria or other microbiological contaminants. However, leakage from a container or exposed surface reduces the chlorine dioxide concentrations at the surface because of chlorine dioxide diffusion into the atmosphere. The chlorine dioxide concentration released from the film for a chosen time period can be calculated given the leakage rate and the rate of absorbance at a surface. Thus after measuring the leakage rate, the composite is formulated so that it contains a large enough reservoir of chlorite reacting at a speed sufficient to compensate for the leakage rate for the desired time period of sustained release.

Detailed Description Text (42):

Therefore, design of a chlorine dioxide releasing composite suitable for controlled

release and biocidal action within a container must take into account several aspects, namely, the chlorine dioxide production rate from the controlled release film, the partitioning of chlorine dioxide between the phases within the container (e.g. gas, liquid and solid phases) in a reversible (absorbed) or irreversible (reacted) fashion, and the leakage rate of gas from the container. Design of such a composite is described in Example 15 of U.S. Pat. No. 5,705,092.

Detailed Description Text (43):

A preferred extended release system of the present invention conserves the chlorite reservoir by emitting a series of periodic pulsed releases timed to coincide with the suspected times of bacterial, viral or fungal contamination or the typical incubation time for the biological of interest. The system design can be optimized to maintain the desired kill concentration for the requisite time at the atmospheric chlorine dioxide leakage rates imposed by the specific application.

Detailed Description Text (46):

It has been discovered that construction of a multilayered composite wherein the arrangement of the layers in the composite is defined by the formula  $C(ACA)_{\text{sub}.n}C$  (wherein  $n$  represents the desired number of pulses) provides periodic pulsed release of high concentrations of chlorine dioxide over several weeks or months. Such pulsed release can be coordinated to the growth, incubation and contamination of viruses, molds, fungi and bacteria. The cycle time and peak concentrations of chlorine dioxide would be controlled by the layer thickness, chlorite and acid releasing polymer loading, and the water and ionic permeation characteristics of layers A and C. Pulsed release occurs as each layer  $(ACA)_{\text{sub}.I}$  is successively penetrated by water vapor and hydronium ions.

Detailed Description Text (49):

Applications for the compositions of the invention are numerous. The water-soluble compositions can be used in most any environment where exposure to moisture will occur so long as the compositions are protected from degradation by a water-insoluble, water-permeable material or are incorporated as a component of a material. The compositions can be used to prevent the growth of molds, fungi, viruses and bacteria on the surface of a material, deodorize the material or inhibit infestation by treating a surface of a substrate with a composition that does not release chlorine dioxide in the absence of moisture, and exposing the treated surface to moisture to release chlorine dioxide from the composition into the atmosphere surrounding the surface. The release of chlorine dioxide retards bacterial, fungal, and viral contamination and growth of molds on the surface, deodorizes the surface, and inhibits infestation. Each component of the composition has a particle size of not more than about 1,000 angstroms.

Detailed Description Text (53):

The compositions of the invention are especially suitable for application to or incorporation in transparent or translucent products. The compositions can also be coated on a surface of a transparent or translucent substrate to provide biocidal action while maintaining the "see-through" quality of the substrate. If the solution is coated onto a clear plastic food container, for example, a consumer can see the food within the container before purchasing the food. The biocidal solution protects the food from microbial contamination while allowing consumers to inspect the food without opening the container. The solution, therefore, allows visual inspection of a material while releasing chlorine dioxide to sterilize, deodorize, or protect the material from contamination or infestation. When the compositions are applied to clear surgical bandages, the wound is sterilized by the chlorine dioxide and is visible through the bandage, allowing for inspection of the wound without removing the bandage and exposing the wound to contamination.

Detailed Description Text (58):

Such a method can also be used to coat the surface of a seed to protect the seed from molds and fungi during storage and to protect against mycotic growth when the seed is planted. The coating, when activated by moisture, creates a microatmosphere of chlorine dioxide in the soil in the vicinity of the seed and inhibits mycotic growth that normally would impede seed germination. This coating has no effect upon the germination of the seeds. Seeds in storage do not have to be physically coated to be protected but rather can be in a closed container containing the active material as a packet, "tea bag" or coating on the container. Paper impregnated with the composite generates sufficient chlorine dioxide to protect the seeds. Although any seeds can be protected by the coating, edible seeds such as corn kernels, sunflower seeds, or soybeans, remain fit for human consumption once they are coated. Thus, the coated seeds can be provided for planting or for human consumption after they have been coated. An optically

transparent composition of the invention can be applied to the seeds to ensure that the appearance of the seeds will not be altered by the composition.

Detailed Description Text (60):

A preferred application includes a foot powder for preventing athlete's foot and other fungi. The powder can be applied directly on the surface of the foot or can be incorporated into a shoe insert. The powder can be applied between the cloth covering and foam pad of the shoe insert, impregnated within the foamed pad, or impregnated or coated on a shoe counter or upper lining. Chlorine dioxide generated from moisture within the shoe diffuses from the composite into the atmosphere to kill fungus and deodorize the shoe. The powder can be blended with conventional ingredients such as talc, cornstarch, fragrance, miconazole nitrate, tolnastate silica, boric acid, aluminum chlorhydrate, salicylic acid, and cellulose. The powder can also be blended with other ingredients and used in bath powders or powders used in treating jock itch.

Detailed Description Text (66):

A polyvinylpyrrolidone oligomer was prepared by polymerizing vinyl pyrrolidinone in water using a free radical initiation with hydrogen peroxide and ammonia catalyst as described by E. S. Barabas, Encyl. Poly. Sci. Eng., 17, 198 (1989). Three grams of vinyl pyrrolidinone were dissolved in seven grams of water and polymerized with 0.03 ml of 30% hydrogen peroxide and 0.3 ml concentrated ammonium water for five hours at 55.degree. C. The reaction products were polyvinylpyrrolidone oligomer and 2-pyrrolidone. At the end of the reaction an additional two ml of 30% hydrogen peroxide was added to oxidize any terminal aldehyde groups to carboxylic acid groups. After solvent was pumped off and the product was vacuum dried at 60.degree. C., a clear, hard polyvinylpyrrolidone oligomer terminated by hydroxyl and carboxyl groups was recovered. The reaction is illustrated below: ##STR15## wherein PVNP represents polyvinylpyrrolidone, which has the formula: ##STR16## wherein n=5 to 500.

Detailed Description Text (68):

A multiblock, polyester copolymer of polyvinylpyrrolidone was prepared by mixing 0.46 g of the polyvinylpyrrolidone oligomer prepared in Example 1, 0.23 g glycolic acid and 0.225 ml of 85% lactic acid with 1.5 ml water and 0.005 g p-toluene sulfonic acid esterification catalyst. The mixture was slowly heated over 20 hours to 120.degree. C. under dynamic vacuum to remove the water of esterification. A multiblock terpolymer having acid end groups was recovered. To esterify the acid end groups, the copolymer was dissolved in a large excess of methanol and neutralized with ammonia. Alternatively, the acid end groups can be esterified with excess methanol. End groups --OR-- rather than the CH.sub.3 O-- end group shown in the reaction scheme below--can be formed by dissolving the polymer in an excess of an alcohol or by dissolving the polymer in an alcohol and neutralizing with ammonia. The alcohol has the formula ROH wherein R is ethyl, n-propyl, or isopropyl. The resultant polyvinylpyrrolidone-poly lactate-glycolate (PVNP-PLGA) terpolymer contained 34 mole % polyvinylpyrrolidone, 32 mole % glycolate and 24 mole % lactate. The preparation of the PVNP-PLGA terpolymer is shown below: ##STR17##

Detailed Description Text (70):

A 30 wt. % solution of the PVNP-PLGA terpolymer prepared according to Example 2 in methanol was neutralized with triethylamine and added to a methanol solution (10 wt. % total solids) of sodium chlorite (recrystallized from methanol), urea and polyvinylpyrrolidone (360,000 MW) so that the total solids mixture contained 51 wt. % PVNP-PLGA terpolymer, 34 wt. % polyvinylpyrrolidone homopolymer, 9 wt. % urea and 6 wt. % sodium chlorite. The solution was cast into a film and remained uniformly dispersed and transparent indefinitely.

Detailed Description Text (72):

A solution of the PLGA copolymer in chloroform was added to a methanol solution (10 wt. % total solids) of sodium chlorite (recrystallized from methanol), urea (10 wt. % total solids) and polyvinylpyrrolidone (360,000 MW). The solution remained cloudy and separated into a PLGA phase and a polyvinylpyrrolidone-urea-chlorite phase when cast into a film.

CLAIMS:

1. A composition for retarding bacterial, fungal and viral contamination and mold growth comprising an acid releasing polymer, a hydrophilic material, and chlorite anions, each component of the composition having a particle size of not more than about 1,000 angstroms, and the composition being substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

10. The composition of claim 5 wherein the chlorite anions are provided by an iminium chlorite or a chlorite salt selected from the group consisting of alkali metal chlorites, alkaline earth metal chlorites, and chlorite salts of a transition metal ion, or a protonated primary, secondary, tertiary or quaternary amine.

11. The composition of claim 1 wherein the acid releasing polymer has a number average degree of polymerization of between about 10 and about 10,000.

12. The composition of claim 11 wherein the acid releasing polymer is a copolymer formed from polyvinylpyrrolidone, polyvinyl alcohol, polyanhydride, or polyacrylamide and at least one .alpha.-hydroxy acid.

13. The composition of claim 12 wherein the copolymer is formed from polyvinylpyrrolidone, lactic acid and glycolic acid.

14. The composition of claim 13 wherein each of the lactic acid, glycolic acid and polyvinylpyrrolidone portions of the copolymer preferably has a number average degree of polymerization of between about 1 and about 5,000.

19. A composition for retarding bacterial, fungal and viral contamination and mold growth comprising an amide, chlorite anions, and an acid releasing terpolymer formed from polyvinylpyrrolidone, lactic acid and glycolic acid, each component of the composition having a particle size of not more than about 1,000 angstroms, and the composition being substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

25. The composition of claim 19 wherein the chlorite anions are provided by an iminium chlorite or a chlorite salt selected from the group consisting of alkali metal chlorites, alkaline earth metal chlorites, and chlorite salts of a transition metal ion, or a protonated primary, secondary, tertiary or quaternary amine.

26. The composition of claim 19 wherein the acid releasing terpolymer has a number average degree of polymerization of between about 10 and about 10,000.

27. The composition of claim 26 wherein the acid releasing terpolymer is formed from polyvinylpyrrolidone, polyvinyl alcohol, polyanhydride, or polyacrylamide and at least one .alpha.-hydroxy acid.

32. A multilayered composite for providing sustained release of chlorine dioxide comprising:

a water-soluble layer comprising an acid releasing polymer, a hydrophilic material and chlorite anions, the layer being substantially free of water and each component of the layer having a particle size of not more than about 1,000 angstroms; and

an upper moisture regulating layer in contact with an upper surface of the water-soluble layer, and a lower moisture regulating layer in contact with a lower surface of the water-soluble layer, the moisture regulating layers being water insoluble, such that moisture permeating either of the moisture regulating layers hydrolyzes the acid releasing polymer to initiate release of chlorine dioxide from the multilayered composite.

33. A multilayered composite for providing time pulsed release of chlorine dioxide comprising:

at least two water-soluble layers comprising an acid releasing polymer, a hydrophilic material and chlorite anions, the layers being substantially free of water and each component of the layers having a particle size of not more than about 1,000 angstroms; and

at least three water-insoluble, water-permeable barrier layers to control the diffusion of water or the diffusion of hydronium ions produced by hydrolysis of the acid releasing polymer into the water-soluble layer;

the arrangement of the layers in the composite being defined by the formula  $C(ACA).sub.n C$  wherein C is a barrier layer, A is a water-soluble layer, and n is an integer ranging from 1 to 10.

34. A process for preparing a composition comprising:

mixing a hydrophilic material, a chlorite salt, an acid releasing polymer and an organic solvent to form a mixture in which each component has a particle size of not more than about 1,000 angstroms, the mixture being substantially free of water and capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

35. The process of claim 34 further including the step of preparing the acid releasing polymer by mixing a polyvinylpyrrolidone oligomer, lactic acid, glycolic acid and water; heating the mixture in the presence of an esterification catalyst to form a polyvinylpyrrolidone lactic acid-glycolic acid terpolymer having acid end groups; dissolving the terpolymer in an organic solvent; and neutralizing the terpolymer to esterify acid end groups of the terpolymer to form the acid releasing polymer.

36. The process of claim 35 wherein the esterification catalyst is p-toluene sulfonic acid.

39. The process of claim 38 further including the step of exposing the film to moisture to hydrolyze the acid releasing polymer and release chlorine dioxide from the composition.

40. The process of claim 38 wherein the composition is applied as a tacky hot melt at a temperature below that at which chlorite within the composition will decompose.

44. A process for preparing a composition comprising:

mixing an amine and an acid releasing polymer to form a mixture; and

exposing the mixture to chlorine dioxide that reacts with the amine to form iminium chlorite within the mixture, the mixture having a particle size of not more than about 1,000 angstroms and being capable of releasing chlorine dioxide upon hydrolysis of the acid releasing polymer.

45. The process of claim 44 wherein the mixture includes a base and, when exposed to chlorine dioxide, the chlorine dioxide reacts with the amine to form iminium chlorite which is decomposed by the base to form a chlorite salt within the mixture.

46. The process of claim 44 wherein the chlorine dioxide dissolves within the amine to form chlorite anions in the mixture.

50. The method of claim 47 wherein the composition is comprised of an acid releasing polymer, a hydrophilic material, and chlorite anions.

56. The method of claim 50 wherein the composition is comprised of an acid releasing polymer and chlorite anions.

59. The method of claim 57 wherein the composition is comprised of an acid releasing polymer and chlorite anions.